

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

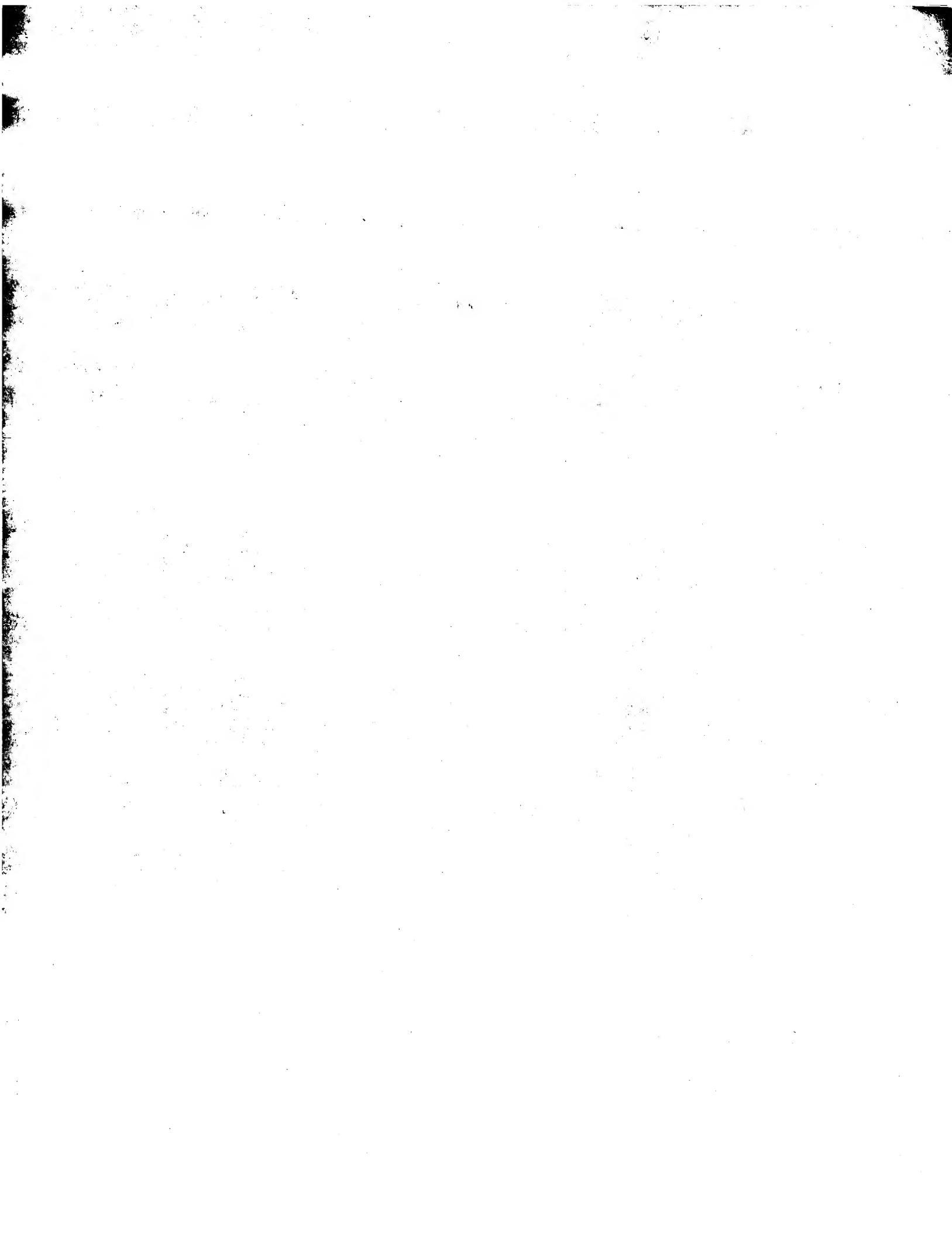
Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.





Europäisches Patentamt

(19) European Patent Office

Office européen des brevets

(11) Publication number:

0092318
A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **83301625.6**

(51) Int. Cl.³: **C 08 L 23/02, C 08 J 5/18**

(22) Date of filing: **23.03.83**

(30) Priority: **26.03.82 US 362103**

(71) Applicant: **Exxon Research and Engineering Company, P.O.Box 390 180 Park Avenue, Florham Park New Jersey 07932 (US)**

(43) Date of publication of application: **26.10.83**
Bulletin 83/43

(72) Inventor: **Janac, Karel Charles, 411 Stanford Avenue, Palo Alto, California (US)**
Inventor: **Puydak, Robert Chester, 17 John Adams Court, Cranbury New Jersey (US)**
Inventor: **Hazelton, Donald Ross, 89 Glenmere Drive, Chatham New Jersey (US)**

(84) Designated Contracting States: **BE DE FR GB IT NL SE**

(74) Representative: **Dew, Melvyn John et al, Esso Chemical Ltd. Esso Chemical Research Centre P.O. Box 1, Abingdon Oxfordshire, OX13 6BB (GB)**

(54) **Blends of polyolefin plastics with elastomeric plasticizers.**

(57) Compositions of matter useful in the preparation of film which is soft and has high tensile, tear and impact strength comprise polyolefin plastics such as polypropylene blended with an elastomeric plasticizer; the latter comprises polyethylene or a copolymer of ethylene and an unsaturated ester of a lower carboxylic acid, olefinic elastomer and a hydrocarbon oil.

EP 0092318 A1

BLENDs OF POLYOLEFIN PLASTICS WITH ELASTOMERIC PLASTICIZERS

1 This invention relates generally to the field of
2 plastics blends or blends of polyolefin plastics with
3 other polymers and, optionally, process aids, fillers,
4 etc. Specifically, it is directed to blends of polyolefin
5 plastics such as polypropylene, polypropylene reactor
6 copolymer, polybutylene, linear low density polyethylene,
7 and high density polyethylene, with a polymeric concen-
8 trate. The polymeric concentrate is preferably elasto-
9 meric in nature and comprises a blend of polyethylene
10 and/or a polymeric copolymer of ethylene, olefinic
11 elastomer, oil and optionally, process aids, antiblock
12 additives, anti-oxidants, fillers, pigments, foaming
13 agents, etc. More specifically, the invention is direc-
14 ted to compositions comprising blends of polypropylene
15 and/or high density polyethylene and an elastomeric
16 plasticizer. The elastomeric plasticizer is readily
17 dispersed and the final compositions can be processed
18 into films on equipment normally intended for low density
19 polyethylene. Films produced from such compositions
20 exhibit low secant modulus, high tear strength and high
21 impact resistance compared to unmodified polyolefin
22 plastics.

23 Polypropylene film is well known in the art, but
24 it is typically produced by the cast or tubular water bath
25 processes rather than employing the less complex equip-
26 ment used for low density polyethylene. Polypropylene
27 film produced using low density polyethylene equipment
28 generally has low impact strength, is very stiff (high
29 secant modulus) and has poor tear strength. Blending
30 polypropylene with various elastomers can improve the
31 impact strength of the polypropylene, but the overall
32 balance of properties is jeopardized, e.g., tensile

1 strength, tear strength, impact resistance and stiffness.
2 More typically, ternary compositions are employed com-
3 prising polypropylene, elastomer and high density poly-
4 ethylene (HDPE) wherein the desired components are di-
5 rectly blended, see, e.g., "Exxon Elastomers for Poly-
6 olefin Modification" (Exxon Chemical Company publication,
7 pages 15-35). This reference suggests that the elastomer
8 and HDPE are incorporated at levels of 5 to 15 weight per-
9 cent. In addition to improved impact strength it is also
10 stated that tensile strength and melt flow rate are de-
11 pressed and, furthermore, there is no teaching that compo-
12 sitions prepared by merely directly blending the indivi-
13 dual components results in a composition which can be pro-
14 cessed on low density polyethylene film equipment.

15 Limited teachings are available which disclose the
16 necessary incorporation of oil in a blend composition such
17 as disclosed herein. However the proportions and proper-
18 ties disclosed in the references are quite different from
19 what is contemplated herein. Furthermore, no reference
20 teaches the unique method of preparing an elastomeric plas-
21 ticizer which is then dispersed in the polyolefin phase,
22 resulting in particularly desirable and useful properties
23 in the final composition. United States Patent 3,957,919
24 describes a thermoplastic elastomer composition which,
25 optionally, can contain extender oil. The composition is
26 hot blended in the presence of a free radical generating
27 catalyst so as to subject the composition to a free radi-
28 cal reaction. The advance represented by this reference
29 is not directed to the subject of the present invention
30 but merely provides a means, specifically the presence of
31 polyethylene (or polyethylene containing 10% or less of
32 copolymerized alpha-olefins having 3 to 16 carbon atoms),
33 in a blend of polypropylene and EPM (ethylene-propylene
34 copolymer) or EPDM (ethylene-propylene terpolymer) which
35 permits the use of a peroxide without significant poly-
36 propylene degradation. Furthermore, the reference spe-

1 specifically describes the preparation of the blend composition as a one step process; such a process is to be contrasted with the method disclosed and claimed herein which utilizes an elastomeric plasticizer concentrate which is blended with the polyolefin plastic. The types of products for which the blend composition is to be used is substantially different in the reference compared with the uses disclosed herein.

9 A later patent to the same inventors, U.S. 4,059,654, 10 discloses the same basic composition and method as above, 11 but the composition contains a slightly higher level of 12 the polyethylene component so as to be better suited for 13 use in the manufacture of flexible hose.

14 Elastomeric thermoplastic compositions containing oil 15 and, optionally, a carbon black filler, for use in molded, 16 paintable structures is disclosed in U.S. 4,132,698. This 17 reference requires the polymeric components to have specific 18 morphological characteristics in order to achieve 19 two discrete, nonhomogeneous, continuous phases. The compositions 20 of the reference differ from those disclosed herein with regard to the content of elastomer component has 22 well as the contemplated uses; the instant compositions 23 being film-forming whereas the reference is directed to 24 molded or extruded articles. Furthermore, the concept disclosed 25 herein of employing an elastomeric plasticizer to achieve 26 unique blend performance properties and process- 27 ability is absent from this and the other references disclosed 28 herein.

29 U.S. Patent No. 4,303,571 teaches the preparation of 30 a film forming blend composition comprising ethylene-propylene 31 elastomers, ethylene-vinyl acetate copolymers and 32 a hydrocarbon oil plasticizer. However, the reference does 33 not recognize that such a composition can be advantageously 34 blended with polyolefin plastics nor, as taught herein, 35 that the method of blending can be particularly beneficial.

1 Compositional differences also distinguish the in-
2 stant invention from other references disclosing thermo-
3 plastic elastomer compositions, for example Japanese Kokai
4 to Sumitomo Chemical, 77 126,450 and Japanese Kokai to
5 Mitsui Petrochemical, 80 71,739. The former reference
6 discloses a modified copolymer rubber composition for use
7 in extruded and molded articles. Additionally, the com-
8 positions of the latter reference are intended to be
9 treated with a peroxide crosslinking agent.

10 In accordance with the present invention, improved
11 compositions of matter have been discovered for use in
12 the preparation of a film which is soft and has high ten-
13 sile, tear and impact strength. The composition is also
14 useful in the production of fibers, tapes, woven fabrics,
15 ropes, etc. The blends are comprised of (a) polyolefin
16 plastics such as polypropylene, polypropylene reactor co-
17 polymer, polybutylene, linear low density polyethylene,
18 high density polyethylene or mixtures thereof (b) poly-
19 ethylene or a copolymer of ethylene and an unsaturated
20 ester of a lower carboxylic acid, (c) olefinic elastomer,
21 and (d) hydrocarbon oil.

22 A particularly advantageous method for preparing the
23 film-forming, thermoplastic elastomeric composition com-
24 prises admixing preformed elastomeric plasticizer with the
25 polyolefin plastics. The elastomeric plasticizer com-
26 prises a blend of components (b), (c) and (d) above.

27 The use of an elastomeric plasticizer is particularly
28 advantageous in that it possesses stable pellet form,
29 blends with polyolefin plastics over broad compositional
30 ranges, and disperses readily under moderate melt mixing
31 conditions.

32 Polyolefin plastics blends useful in this invention
33 can employ polypropylene which can be a highly crystalline
34 isotactic or syndiotactic polypropylene. Also, the poly-

1 propylene may be a copolymer, referred to as a polypropy-
2 lene reactor copolymer, either random or block copolymer,
3 containing minor amounts of an alpha-olefin comonomer of
4 2 to 16 carbon atoms. The level of comonomer which can be
5 utilized is about 1 to about 20 weight percent, prefer-
6 ably about 2 to about 18, most preferably about 2 to about
7 15; a preferred comonomer is ethylene. The density of
8 polypropylene can be from about 0.800 to about 0.900 g/cc.
9 High density polyethylene (HDPE) useful as the polyolefin
10 plastic to be blended with the elastomeric plasticizer
11 has a density of about 0.941 to about 0.965 g/cc. High
12 density polyethylene is an established product of com-
13 merce and its manufacture and general properties are well
14 known in the art. Typically, HDPE has a relatively broad
15 molecular weight distribution, characterized by the ratio
16 of weight average to number average molecular weight, of
17 from about 20 to about 40. HDPE for use in film can have
18 a melt index (ASTM D1238, Method E) of from about 0.03 to
19 about 5.0 g/10 min. and a density of from about 0.941 to
20 about 0.965 g/cc.

21 Polybutylene, which is also useful in this invention,
22 as the polyolefin plastic, is a term which generally re-
23 fers to both poly (1-butene) homopolymer and the copolymer
24 with, e.g., ethylene, propylene, pentene-1, etc. Particu-
25 larly useful in this invention is the ethylene copolymer.
26 Polybutylene is manufactured via stereospecific Ziegler-
27 Natta polymerization of the monomer(s). Commercially use-
28 ful products are of high molecular weight and isotacti-
29 city. A variety of commercial grades of both homopolymer
30 and ethylene copolymer are available with melt indices
31 that range from about 0.3 to about 20 g/10 min.; commer-
32 cial ethylene copolymer grades have a melt index of from
33 about 1 to about 2, although it is to be expected that a
34 wider range would be acceptable, e.g., from about 0.5 to
35 about 5 or higher, depending on the intended application.

1 Linear low density polyethylene (LLDPE) is a relatively new class of low density polyethylene characterized by little, if any, long chain branching, in contrast to conventional low density polyethylene. The processes for producing LLDPE are well known in the art and commercial grades of this polyolefin plastic are available. 7 Generally, it is produced in gas-phase fluidized bed reactors or liquid-phase solution process reactors; the former process can be carried out at pressures of about 10 100 to 300 psi and temperatures as low as 100° C. Polymers can be made in the gas phase with melt indices and 11 densities over the full commercial range and with molecular weight distributions from very narrow to very broad. 12 Typically, the level of polyolefin plastics employed is 13 from about 95 to about 15 weight percent of the composition, preferably about 92 to about 17 weight percent, 14 most preferably about 90 to about 20 weight percent.

15 The elastomeric plasticizer comprises, in part, a 16 polyethylene component which can be low density polyethylene (for example, about .910 to about .925 g/cc), medium 17 density polyethylene (for example, about .925 to about 18 .940 g/cc) or high density polyethylene (for example, 19 about .941 to about .965 g/cc). The polyethylene can be 20 prepared by a high pressure process or a low pressure process 21 and includes linear polyethylene and copolymers of 22 ethylene. The term polyethylene as used herein also 23 includes polyethylene copolymers such as copolymers of 24 ethylene and alpha-olefins having 3 to 16 carbon atoms, 25 for example, propylene, 1-butene, etc, as well as co- 26 polymers of ethylene with an unsaturated ester of a lower 27 carboxylic acid. In particular, copolymers of ethylene 28 with vinyl acetate or alkyl acrylates, for example, methyl 29 acrylate and ethyl acrylate, are employed. For the purposes 30 of this invention, polyethylene copolymers are also 31 considered to include blends of polyethylene and polyethylene 32 copolymers. The polyethylene copolymers to be employed 33 generally contain from about 50 to about 99 weight 34 35 36 37

1 percent ethylene, preferably about 60 to about 95 weight
2 percent ethylene, most preferably about 70 to about 90
3 weight percent ethylene. The level of polyethylene or
4 polyethylene copolymer employed in the final blend compo-
5 sition is generally from about 2 to about 60 weight per-
6 cent of the composition, preferably from about 3 to about
7 50 weight percent, most preferably about 4 to about 40
8 weight percent, for example from about 5 to about 35
9 weight percent.

10 The olefinic elastomer component of the elastomeric
11 plasticizer can comprise ethylene copolymer elastomers,
12 such as copolymers of ethylene with higher alpha-olefins
13 such as propylene. The ethylene elastomer copolymers for
14 use herein should include between about 30 and about 90
15 weight percent ethylene, preferably between about 35 and
16 about 80 weight percent ethylene, most preferably between
17 about 50 and about 70 weight percent ethylene. In some
18 cases an oil extended elastomer can be employed in the
19 compositions of this invention. In such case, the com-
20 position is adjusted to take account of the oil added by
21 means of the oil extended elastomer as compared to the
22 total amount of oil desired in the final composition.

23 It is also within the scope of this invention to
24 employ as the olefinic elastomer an ethylene copolymer
25 elastomer comprising a terpolymer of ethylene, a higher
26 alpha-olefin such as propylene, and a nonconjugated diene
27 (the terpolymer commonly referred to as EPDM). In such
28 elastomers the nonconjugated diolefin may be straight
29 chain, branched chain or cyclic hydrocarbon diolefins
30 having from 6 to 15 carbon atoms, such as the following:

31 A. straight chain acyclic dienes such as: 1,
32 4-hexadiene; 1, 6-octadiene;
33 B. branched chain acyclic dienes such as:
34 5-methyl-1, 4-hexadiene; 3,7-dimethyl-1,6-octa-
35 diene; 3,7-dimethyl-1,7 octadiene and the mixed
36 isomers of dihydro-myrcene and dehydro-ocinene;

1 C. single ring alicyclic dienes such as: 1,3-
2 cyclopentadiene; 1,4-cyclohexadiene; 1,5-cyclo-
3 octadiene; and 1,5-cyclododecadiene;
4 D. multi-ring alicyclic fused and bridged ring
5 dienes such as: tetrahydroindene; methyltetra-
6 hydroindene; dicyclopentadiene; bicyclo-(2,2,1)-
7 hepta-2,5-diene; alkenyl, alkylidene, cyclo-
8 alkenyl and cycloalkylidene norbornenes such as
9 5-methylene-2-norbornene (MNB), 5-ethylidene-2-
10 norbornene (ENB), 5-propenyl-2-norbornene, 5-
11 isopropylidene-2-norbornene, 5-(4-cyclopentenyl)-
12 2-norbornene; 5-cyclohexylidene-2-norbornene;
13 5-vinyl-norbornene; and norbornadiene.

14 Of the non-conjugated dienes typically used to prepare
15 these copolymers, preferred are dicyclopentadiene, 1,4-
16 hexadiene, 5-methylene-2-norbornene and 5-ethylidene-2-
17 norbornene; 5-ethylidene-2-norbornene (ENB) and 1,4-hexa-
18 diene are particularly preferred diolefins. EPDM elasto-
19 mers and their method of manufacture are now well known to
20 those skilled in the art. Oil extended EPDM elastomers are
21 also within the scope of disclosed EPDM elastomers. Pre-
22 ferred EPDM elastomers contain about 30 to about 90 weight
23 percent ethylene, more preferably about 35 to about 80
24 weight percent ethylene, most preferably about 50 to about
25 70 weight percent ethylene, and from about 0.5 to about 15
26 weight percent nonconjugated diolefin, e.g., ENB.

27 The olefinic elastomer useful in this invention can
28 also be polyisobutylene, copolymers of isobutylene and iso-
29 prene (generally known as butyl rubber) and halogenated co-
30 polymers of isobutylene and isoprene (generally known as
31 halogenated butyl rubber, such as chlorinated, brominated
32 and chlorobrominated butyl rubber). Butyl rubber is a vul-
33 canizable rubbery copolymer containing from about 85 to
34 99.5 percent combined isoolefin having from 4 to 8 carbon
35 atoms and 0.5 to 15 percent combined conjugated diolefin
36 having from 4 to 8 carbon atoms. Such copolymers and their
37 preparation are well known, and generally the isoolefin is

1 a compound such as isobutylene and the diolefin is a com-
2 pound such as butadiene or isoprene. Halogenated butyl
3 rubber is also well known; chlorinated and brominated
4 butyl rubber generally contain at least about 0.5 weight
5 percent combined halogen and up to about 1 atom of halo-
6 gen per double bond in the copolymer; chlorobrominated
7 butyl rubber generally contains from about 1.0 to about
8 3.0 weight percent bromine and from about 0.05 to about
9 0.5 weight percent chlorine.

10 The level of olefinic elastomer employed in the final
11 blend composition is generally from about 1 to about 50
12 weight percent of the composition, preferably from about
13 2 to about 40 weight percent, most preferably about 3 to
14 about 30 weight percent.

15 A hydrocarbon oil is also incorporated into the ther-
16 moplastic elastomeric blend composition as a component of
17 the elastomeric plasticizer. The hydrocarbon oils which
18 can be used include aromatic, naphthenic and paraffinic
19 types. Aromatic oils are less preferred in some applica-
20 tions because of potential color limitations and regula-
21 tions of the United States Food and Drug Administration,
22 especially where the film or finished product comes into
23 contact with food. For certain applications an especially
24 "clean" oil may be preferred, such as a white mineral oil,
25 a petroleum hydrocarbon oil (e.g., Primol, marketed by
26 Exxon Company, USA). The level of hydrocarbon oil em-
27 ployed in the final blend composition is generally from
28 about 1 to about 30 weight percent of the composition,
29 preferably from about 2 to about 20 weight percent, most
30 preferably from about 3 to about 15 weight percent.

31 Considering the elastomeric plasticizer independently
32 of the total (or final) thermoplastic elastomeric blend
33 the preferred amount of polyethylene or copolymer of
34 ethylene would be about 20 to about 70 weight percent of
35 the elastomeric plasticizer, the olefinic elastomer from
36 about 20 to about 80 weight percent and the hydrocarbon
37 oil from about 1 to about 35 weight percent.

1 A further embodiment of this invention is the incor-
2 poration into the elastomeric plasticizer composition of
3 a small percentage of polyolefin plastics, such as poly-
4 propylene, polypropylene reactor copolymer, polybutylene,
5 linear low density polyethylene, high density polyethylene
6 or mixtures thereof, in order to improve the storage sta-
7 bility and ease of handling of the elastomeric plasticizer.
8 Useful levels of such polyolefin plastic would be up to
9 about 30 weight percent, preferably up to about 20 weight
10 percent, most preferably up to about 15 weight percent,
11 for example, up to about 10 weight percent based on the
12 weight of the elastomeric plasticizer. The proportions of
13 elastomeric plasticizer and polyolefin plastics are ad-
14 justed for the final composition in order to take into
15 account the polyolefin plastic present in the elastomeric
16 plasticizer.

17 In addition to the essential ingredients of the over-
18 all thermoplastic elastomeric composition (polyolefin
19 plastic and elastomeric plasticizer as previously defined)
20 as well as the optional use of a small percentage of poly-
21 olefin plastic in the elastomeric plasticizer (as previous-
22 ly disclosed), various optional ingredients can be incor-
23 porated into the composition in order to achieve various
24 cost and/or performance objectives in specific end-use
25 applications. For example, one can use such materials as
26 process aids (e.g., stearic acid), lubricants (e.g., ole-
27 amide), antiblocking aids, antioxidants, foaming agents
28 and fillers and pigments. The latter two classes of ma-
29 terials can be used at levels up to about 40 weight per-
30 cent based on the weight of the total composition.

31 Preparation of compositions of this invention, i.e.,
32 the blend of polyolefin plastics and elastomeric plasti-
33 cizer as described above, can be achieved in several dif-
34 ferent ways. The polyolefin plastics and elastomeric plas-
35 ticizer are brought into intimate contact by, for example,
36 dry blending these materials and then passing the overall
37 composition through a compounding extruder. Alternatively,

1 the polyolefin plastics and elastomeric plasticizer can
2 be fed directly to a mixing device such as a compound-
3 ing extruder, high shear continuous mixer, two roll mill,
4 an internal mixer such as a Banbury, etc. The optional
5 ingredients previously described can be added to the com-
6 position during this mixing operation. It is also pos-
7 sible to achieve melt mixing in an extruder section of a
8 film line or in an injection molding machine. Overall,
9 the objective is to obtain a uniform dispersion of all
10 ingredients and this is readily achieved by inducing suf-
11 ficient shear and heat to cause the plastics component(s)
12 to melt. However, time and temperature of mixing should
13 be controlled as is normally done by one skilled in the
14 art so as to avoid molecular weight degradation and un-
15 necessary volatilization of oil. Depending on the poly-
16 olefin plastics component(s) employed, a melt temperature
17 range of about 250°F to about 550°F could be expected.
18 Where extruder mixing is employed the length to diameter
19 (L/D) ratio of the screw should be at least 10/1, prefer-
20 ably at least 15/1.

21 Generally, the elastomeric plasticizer is prepared
22 in a separate operation from the preparation of the final
23 composition. However, it should be recognized that it is
24 possible to separate these steps only minimally so that a
25 sequential two stage batch process produces the final
26 composition or alternatively, a continuous process can be
27 achieved by using, for example, a mixing extruder with
28 multiple feed sections.

29 Where it is preferred to prepare the elastomeric
30 plasticizer as a separate operation, process conditions
31 known to those skilled in the art are followed in order
32 to obtain uniform dispersion of the ingredients. The
33 elastomeric plasticizer can advantageously be prepared
34 in pellet form so that it can be fed into the final mix-
35 ing stage, with the olefinic plastics, using plastics
36 pellet metering equipment.

1 Preparation of the elastomeric plasticizer is readi-
2 ly achieved by using mixing equipment well known in the
3 art so as to obtain high shear. For example, such mix-
4 ing can be obtained in an internal mixer such as a
5 Banbury, on a two roll mill, in a continuous mixing ex-
6 truder, high shear continuous mixer, etc. Those skilled
7 in the art are familiar with the principles of controlling
8 time, temperature and sequence of ingredients so as to
9 maximize uniformity of dispersion of the ingredients in
10 the composition. Pelletization of the elastomeric plas-
11 ticizer can be carried out after mixing and is preferred
12 so that such pellets can readily be handled and subse-
13 quently conveniently blended with pellets of the poly-
14 olefin plastics in order to prepare the final composition.

15 It is recommended that the melt temperature of the
16 elastomeric plasticizer be kept under 450°F during its
17 preparation to minimize liberation of acetic acid (where
18 ethylene vinyl acetate is used in the formulation). It
19 is generally most convenient to mix the elastomeric plas-
20 ticizer in a two-step Banbury mixing operation, especially
21 if it is desirable to minimize the amount of undispersed
22 particles of olefinic elastomers in the final film. The
23 first pass is typically used to blend the olefinic elas-
24 tomer and polyethylene or copolymer of ethylene as pre-
25 viously defined, and the second is used to extend the mix-
26 ture with the oil and other ingredients (e.g., processing
27 aids, fillers, etc.). Dump temperatures are typically
28 320°F - 380°F for the final oil-containing mixture.

29 Following preparation of the final composition (poly-
30 olefin plastics plus elastomeric plasticizer and optional
31 ingredients), the blend can be used to manufacture the
32 unique film which results. Where polypropylene is the
33 polyolefin, soft polypropylene films can be produced
34 which are processable on low density polyethylene blown
35 and cast equipment without any modifications. It can
36 also be used on other types of equipment commonly used
37 to produce plastic films, e.g., tubular water bath

1 extrusion process, blown or cast co-extrusion process, ex-
2 trusion coating onto another substrate, etc.

3 Since the elastomeric plasticizer disperses readily
4 in the polyolefin plastics in all proportions cited here-
5 in, even under moderate melt mixing conditions, mixing
6 can be achieved just prior to end use, for example, in
7 the extruder section of a film line or an injection mold-
8 ing machine.

9 Film produced according to the compositions and
10 methods taught herein has excellent drawability, with
11 high quality film being obtained at gauges as low as 0.5
12 mil; it is expected that high quality film can be obtain-
13 ed in gauges even as low as 0.3 mil. The films have a
14 low secant modulus, high tear strength, impact and punc-
15 ture resistance, while having good temperature resistance
16 and high tensile strength contributed by the polyolefin
17 plastics.

18 In addition to film, the compositions disclosed
19 herein can be used to prepare fibers, tapes, woven fabrics,
20 ropes, and products made by injection molding, blow mold-
21 ing, sheet forming, thermoforming, extruding etc., having
22 especially in comparison to polypropylene increased flex-
23 ibility, decreased splittiness and fibrillation, improved
24 heat sealing, and improved absorption of inks and dyes.

25 The scope and significance of the present invention
26 may be more fully understood with reference to the follow-
27 ing specific examples thereof.

28 EXAMPLE 1

29 Polypropylene and low density polyethylene films were
30 prepared and properties compared to blend compositions of
31 the present invention, i.e., polypropylene containing elastomeric
32 modifier. In one experiment (Table I(d)) the elastomeric
33 plasticizer was a blend of 49% ethylene methyl acrylate
34 (PE-2205, 2.4 MI@190°C, 0.942 g/cc density) 28% ethylene
35 propylene rubber (Vistalon 3708, 65% ethylene, 3.7% ENB)
36 20% oil, 2% slip agent (Oleamide) and 1% stearic acid.

1 To prepare the plasticizer, resin and elastomer were
2 fluxed in a 1D size Banbury for 1 minute. After 2 minutes
3 of mixing the oil was added and the mixture attained flux
4 conditions again after 4½ minutes. At 5 minutes, the
5 other materials were added and the batch was dropped at
6 295°F in 6½ minutes. The blend was then strand cut,
7 pelletized and Banbury mixed 4½ minutes with the poly-
8 propylene (grade SA-861) reaching a dump temperature of
9 380°F. In experiment (e) of Table I a similar elasto-
10 meric plasticizer composition was prepared as an experi-
11 ment (d), it was blended 50/50 with polypropylene as
12 described above and used to produce a cast film. Film
13 properties of the compositions of this invention are
14 summarized in Table I and compared to unmodified poly-
15 olefin Plastics films.

16 EXAMPLE 2

17 This example shows the effect of elastomeric plas-
18 ticizer concentration in a polypropylene blend on
19 several properties of extruded melt drawn tapes (Table
20 II). The elastomeric plasticizer contained 51% UE-631,
21 28% VISTALON 3708, 20% Primol 355, and 1% stearic acid.
22 Its method of preparation was similar to that cited in
23 Example 1. The polypropylene grade used was Escorene PP
24 1012, an injection molding resin having a density of
25 0.900 g/cc and a melt flow rate of 5.3 at 230°C (condi-
26 tion L).

27 EXAMPLE 3

28 The effect on blown film properties of varying the
29 composition of the elastomeric plasticizer is shown
30 in this example. The polypropylene grade remained con-
31 stant as did the blend ratio of polypropylene and
32 elastomeric plasticizer (60/40). Film properties are
33 shown in Table III; MD refers to machine direction, TD to
34 transverse direction. The elastomeric plasticizer and
35 the blend with polypropylene were prepared as previously
36 described in Example 1.

1 EXAMPLE 4

2 In this example high molecular weight, high density
3 polyethylene (HDPE, grade Hostalen \circledR 9255F) was used as
4 the polyolefin plastic. Pellets of HDPE were dry blended
5 with an elastomeric plasticizer (in the ratio 75 HDPE:
6 25 elastomeric plasticizer) comprising:

7 Ethylene vinyl acetate (14 wt.% vinyl acetate,
8 grade UE 622) - -48%
9 EPDM rubber (65 wt.% ethylene, grade, Vistalon
10 3708) -28%
11 Oil (grade, Arco \circledR Prime 400) -23%
12 Stearic Acid - 1%

13 The dry blended composition was passed through a 2 $\frac{1}{2}$
14 inch dia. Royle compounding extruder and blown into a film
15 using a 2 $\frac{1}{2}$ in. dia. Alpine extruder. Surprisingly, it was
16 possible to produce a 1 mil gauge film with the composi-
17 tion of this invention. Compared to prior art film compris-
18 ing a blend of HDPE and polyisobutylene the film of this
19 invention produced in this example showed better clarity,
20 less tendency to stress whiten when creased and higher
21 machine direction tear strength in a 4 mil film. Proper-
22 ties are summarized in Table IV.

23 EXAMPLE 5

24 The experiment of Example 4 was repeated except that
25 1 mil films were prepared and properties of the blend of
26 high molecular weight HDPE with the elastomeric plasti-
27 cizer were compared with controls of unplasticized HDPE;
28 one was the high molecular weight plastic used in the blend
29 and a second, a medium molecular weight HDPE. Data are
30 summarized in Table V.

31 EXAMPLE 6

32 The addition of elastomeric plasticizer to polybuty-
33 lene (grade 8640, an ethylene-1-butene copolymer, MI=1.0
34 at 190°C) was evaluated using a conventional low density
35 polyethylene blown film line. The formulation of the
36 elastomeric plasticizer corresponds to that used in Example
37 3 and its method of preparation was as described in

- 16 -

1 Example 1. The plasticizer concentrate was dry blended
2 with pellets of polybutylene in ratios of 75:25 and 50:50
3 polybutylene:plasticizer and fed directly to the hopper
4 of a 1-1/2 inch, 24:1 L:D extruder. The elastomeric plas-
5 ticer dispersed well in the polybutylene and the bubble
6 demonstrated greater stability over straight polybutylene.
7 Properties of the resulting films are given in Table VI.
8 The films exhibited high toughness, greater clarity, and a
9 softer feel relative to neat polybutylene.

10 EXAMPLE 7

11 This example describes the use of polyisobutylene
12 (grade VISTANEX [®] L-80) as a component of the elastomeric
13 plasticizer. The elastomeric plasticizer was prepared
14 in a Banbury mixer according to mixing procedures describe
15 earlier. It was then underwater-pelletized using a 2½
16 inch, 24:1 L:D extruder.

17 The plasticizer pellets were then dry blended with
18 polypropylene (grade-Escorene PP 5052) in the ratio 60PP:
19 40 elastomeric plasticizer and underwater-pelletized, again
20 using a 2½ inch extruder. Film was blown on a commercial
21 1½ inch LDPE blown film line using a die gap of 23 mils.
22 The film processed easily and resulted in the properties
23 indicated in Table VII.

24 EXAMPLE 8

25 An elastomeric plasticizer of the following formu-
26 lation: 37% UE-622 EVA, 12% UE-645 (28% vinyl acetate,
27 1.0 MI), 28% VISTALON 3708, 23% Primol 355, and 0.2%
28 Irganox 1076, was extruder mixed at a 75:25 ratio with
29 linear low density polyethylene (LLDPE, grade LPX-1, 1.0
30 MI, 0.918 g/cc) and processed into film on a conventional
31 low density polyethylene line using a die gap of 23 mils.
32 The plasticizer had been Banbury mixed and pelletized as
33 previously described. Unlike neat LLDPE, which normally
34 requires wider die gap settings and a specialized screw
35 design, the plasticized LLDPE processed well on the un-
36 modified equipment.

0092318

17

TABLE I
PROPERTIES OF 1 MIL FILMS

EXPERIMENT	<u>a</u>		<u>b</u>		<u>c</u>		<u>d</u>		<u>e</u>	
	PP (1)	PP (2)	LDPE (3)	LDPE (4)	60 X PP (5)	60 X PP (6)	50X PP (3)	50X PP (5)	50X PP (6)	
Polyolefin Plastic										
Elastomeric Plasticizer	—	—	—	—	—	—	—	—	—	
Film Type	Blown	Cast	Blown	Blown	Blown	Blown	Cast	Cast	Cast	
Blow Up Ratio	3.1	—	2.55	2.55	—	—	—	—	—	
Gauge, mils	1.1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	
Yield Strength, Psi Machine (H)	5230	3400	1430	1596	1519	1519	—	—	—	
ASTM - D882	Transverse (T)	—	3400	1565	1519	1519	—	—	—	
Elongation at Yield H	15	10	10	25	—	—	—	—	—	
ASTM - D882, X T	—	10	10	20	—	—	—	—	—	
Tensile Strength, Psi H	6170	7000	2397	5179	6379	6379	—	—	—	
ASTM - 882 T	3320	7000	3849	4722	3932	3932	—	—	—	
Ultimate Elongation, % H	505	700	420	640	640	640	—	—	—	
ASTM - D1922 T	10	700	155	655	690	690	—	—	—	
1X Secant Modulus, Psi H	168,100	110,000	32,567	36,500	28,570	28,570	—	—	—	
ASTM - D882 T	185,000	110,000	—	—	—	—	24,300	—	—	
Klemendoff Test, g/mm H	6	30	126	—	—	—	—	—	—	
ASTM - D1922 T	9	100	56	—	—	—	112	—	—	
Bent Drop Impact, Grams	10	100	—	—	—	—	320	—	—	
ASTM - D1709 (PP30)	—	—	—	—	—	—	360	—	—	

22
 23 (1) Polypropylene-grade Proflex PD 064
 23 (2) Polypropylene-grade Proflex PD 742
 24 (3) Low Density Polyethylene-grade LD-130
 25 (4) Polypropylene-grade SA-861
 26 40% Elastomeric Plasticizer (19.6% EHA 2205, 11.2% VISTALON 2708, 0.8% Oleamide, 0.4% stearic acid)
 27 (5) 50% Polypropylene-grade SABOL, 50% Elastomeric Plasticiser (24.5% EVA-UE-631, 14% VISTALON 2708, 10% PMIOL 355, 0.5% stearic acid, 1% Oleamide)

1

TABLE II

2

PROPERTIES OF EXTRUDED MELT-DRAWN TAPES

3	<u>COMPOSITION</u>	<u>a</u>	<u>b</u>	<u>c</u>
4	POLYPROPYLENE	85	70	50
5	ELASTOMERIC PLASTICIZER	15	30	50
6	<u>MELT INDEX AT 190°C</u>	2.5	3.5	3.0
7	<u>MELT FLOW RATE AT 230°C</u>	5.1	7.0	7.5
8	PHYSICAL PROPERTIES OF			
9	<u>EXTRUDED MELT-DRAWN TAPES</u>			
10	TENSILE AT YIELD, PSI	3190	2260	1580
11	ELONGATION AT YIELD, %	15	18	25
12	ULTIMATE TENSILE, PSI	5600	5300	5100
13	ULTIMATE ELONGATION, %	725	810	875
14	STIFFNESS		<u>DECREASING</u> →	
15	SHORE D HARDNESS	60	55	42

0092318

19

TABLE III
(1)

EXPERIMENT		OIL EXTENDED EPDM (3)	EP COPOLYMER (4)	ETHYLENE-HEXYL ACRYLATE COPOLYMER (5)		LOW DENSITY POLYETHYLENE (6)	ETHYLENE VINYL ACETATE COPOLYMER (7)
4	5			b	c		
6	Avg. Gauge, mils	1.1	1.1	1.0	1.1	1.1	1.2
7	BLOW UP RATIO	2.55	2.55	2.55	2.55	2.55	2.55
8	HOOOLUS AT YIELD, PSI HD	1462	1718	1596	2284	1603	
9	TD	1466	1731	1519	1974	1450	
10							
11	ELONGATION AT YIELD, % ID	25	25	25	35	30	
12	TD	20	20	20	25	20	
13							
14	10X MODULUS, PSI TD	1262	1590	1339	1784	1299	
15							
16	25X MODULUS, PSI ID	1462	1718	1596	2264	1591	
17							
18	TENSILE STRENGTH, HD PSI	2774	4381	5179	5132	4364	
19	TD	4076	4783	4722	4379	3732	
20							
21	SECANT MODULUS, PSI	30,433	39,100	36,500	47,500	40,167	
22							
23	ELONG. % ID	625	640	640	590	595	
24	TD	675	675	655	640	655	
25							
26							
27	(1) 60% POLYPROPYLENE, 40% ELASTOMERIC PLASTICIZER						
28	(2) Base Formula: 49% EVA-UR-611, 20% VISTALON 3700, 20% PRIMOL 315, 2% o-camphor, 1% stearic acid						
29	(3) EP-2105 TERPOLYMER, 75 ph oil, 66 wt % ethylene (Grade-Vistalon 719)						
30	(4) Ethylene-77 wt % (Grade-Vistalon 719)						
31	(5) EP-2205, 2.4 dg/min HI at 170°C, 0.942 g/cc density						
32	(6) Escorane LD-106, 2.8 HI at 190°C, 0.919 g/cc density, 106.5 °C HF						
33	(7) Vinyl acetate-9% (Grade-Zacorene LD-401, 3.4 HI at 190°C, 0.919 g/cc density)						

<u>TABLE IV</u> <u>HIGH DENSITY POLYETHYLENE FILMS</u>						
(1)						
4	HDPE: 0.4 MI	100	80	70	60	-
5	0.1 MI	-	-	-	-	75
6	Polyisobutylene	-	20	30	40	-
7	Elastomeric Plasticizer	-	-	-	-	25
8						
9	<u>Average Gauge, mils</u>	4.0	4.0	4.0	4.0	3.78
10	<u>Tensile Strength, psi</u>					
11	@ Yield MD	3800	2700	2100	1700	2500
12	ID	4200	2700	2100	1500	2550
13	@ Break MD	-	-	-	-	5100
14	ID	-	-	-	-	5100
15	<u>Elongation, %</u>					
16	@ Yield MD	10	15	15	20	20
17	@ ID	10	10	10	10	20
18	@ Break MD	-	-	-	-	760
19	ID	-	-	-	-	750
20	<u>1% Secant Modulus, psi</u>					
21	MD	116,000	87,000	64,000	48,000	63,400
22	ID	148,000	91,000	68,000	50,000	68,200
23	<u>Elmendorf Tear, g/mil</u>					
24	MD	20	50	70	120	270
25	ID	40	200	350	>360	400
26	<u>Dart Drop Impact, F₅₀, gm</u>					
27	1 1/2" dart, 26 inch drop	150	540	700	940	560

28 (1) HDPE/polyisobutylene films - Source of Data: "Exxon Elastomers for Polyolefin Modification". HDPE-0.4 melt index;
29 Polyisobutylene-grade, Vistanex \textcircled{B} L-120
30

0092318

TABLE Y

BLOCK SOFT HDPE FILM		HDPE Controls (1)		High Mol. Wt. HDPE With Elastomeric Plasticizer	
	High Mol. Wt. WPE	High Mol. Wt. WPE	High Mol. Wt. WPE	High Mol. Wt. WPE	High Mol. Wt. WPE
6	Average Gauge, mils	0.92	0.98	0.98	1.0
7	Tensile Strength, psi				
8	@ Yield HD	1820	4650	3450	
9	TD	1600	1950	3350	
10	@ Break HD	8450	7100	8350	
11	TD	4700	6750	5800	
12	Elongation, %				
13	@ Yield HD	10	10	10	
14	TD	10	10	10	
15	@ Break HD	510	470	470	
16	TD	690	490	630	
17	1% Secant Modulus, psi				
18	HD	120,900	156,800	161,100	
19	TD	166,100	166,100	161,300	
20	Elemental Tear, g/100 mil				
21	HD	30	40	30	
22	TD	520	60	360	
23	Dart Drop Impact, ft-lbs (2)				
24		430	105	97	
25	Puncture Impact, lb-in/mil				
26	Hard, %	410	540	500	
27	Close 45°, %	88	89	34	
28		4	4	15	
29	(1) Hrd. Mol. Wt. = ALATON 7815 (MFI = 0.4); High Mol. Wt. = HOSTAFLEX 9255P (MFI = 0.1)				
30	(2) P50 Method 1 1/2" dart, 26" drop				

1

TABLE VI

2

Properties of

3

POLYBUTYLENE BASED BLOWN FILMS

4

Polybutylene 8640, % 100 75 50

5

Elastomeric Plasticizer, % - 25 50

6

Average Sample Gauge, mils 3.95 3.5 4.1

7

100% Modulus, psi MD 2955 2403 1696
TD 2333 1997 1504

9

300% Modulus, psi MD 5686 4496 3063
TD 4023 3634 2628

10

Modulus at 1% Extension, psi 382 171 142

11

Tensile Strength at Break, MD 6482 5573 4211
psi TD 5264 5232 3645

12

% Elongation at Break MD 355 415 490
TD 410 485 475

13

Elmendorf Tear Strength
(ASTM D-1922), g/mil (1)

14

MD - 308 NT

15

TD - 444 NT

16

20

21

(1) No Tear

1

TABLE VII

2

PROPERTIES OF MODIFIED
(1)
POLYPROPYLENE FILM (BLOWN)

5

Average Gauge, mils 1.0 3.8

6

Tensile Strength, psi
@ Yield MD 2,712 2,318
TD 2,373 2,476

9

@ Break MD 6,780 5,545
TD 4,745 5,523

11

Elongation, %
@ Yield MD 25 25
TD 25 25

14

@ Break MD 570 720
TD 505 665

16

1% Secant Modulus, psi
MD - 47,830
TD - 40,910

19

Elmendorf Tear, g/mil
MD 78 85
TD 192 76

22

(1) Polypropylene 60%, Elastomeric plasticizer 40%. Poly-
propylene grade: Escorene PP 5052, 1.2 MFR (Condition L);

25

Elastomeric Plasticizer: 49% UE-645 (28% VA content, 1.2 MI),
28% VISTANEX L-80, 23% Primol 355, 0.2% Irganox 1076.

CLAIMS

1. A film-forming, thermoplastic elastomeric blend composition comprising:
 - (a) a polyolefin plastics component selected from polypropylene, polypropylene reactor copolymer, polybutylene, linear low density polyethylene, high density polyethylene, and mixtures thereof; and an elastomeric plasticizer comprising:
 - (b) polyethylene or a copolymer of ethylene and an unsaturated ester of a lower carboxylic acid,
 - (c) an olefinic elastomer, and
 - (d) a hydrocarbon oil.
2. A composition according to claim 1 characterised in that said olefinic elastomer is selected from ethylene copolymer elastomers, ethylene terpolymer elastomers, polyisobutylene, and isoprene copolymer elastomers including isobutylene-isoprene copolymer elastomers and halogenated isobutylene-isoprene copolymer elastomers.
3. A composition according to claim 2 characterised in that said olefinic elastomer comprises a copolymer of ethylene and propylene, or a terpolymer of ethylene, propylene and a non-conjugated diene.
4. A composition according to claim 1, 2 or 3 characterized in that component (b) is selected from high density polyethylene, low density polyethylene, linear low density polyethylene, vinyl esters and alkyl acrylates.
5. A composition according to claim 4 characterized in that component (b) is a vinyl ester comprising vinyl acetate or an alkyl acrylate selected from methyl acrylate and ethyl acrylate.

6. A composition according to any one of the preceding claims characterized in that said hydrocarbon oil is selected from paraffinic, naphthenic and aromatic oils.
7. A composition according to any one of the preceding claims which comprises from 15 to 95 weight percent of said component (a), based on the total composition.
8. A composition according to any one of the preceding claims which comprises from 2 to 60 weight percent of said component (b), based on the total composition.
9. A composition according to any one of the preceding claims which comprises from 1 to 50 weight percent olefinic elastomer, based on the total composition.
10. A composition according to any one of the preceding claims which comprises from 1 to 30 weight percent hydrocarbon oil, based on the total composition.
11. A method of producing a film-forming thermoplastic elastomeric blend composition according to any one of the preceding claims which comprises providing the polyolefin plastics component (a) and a preformed elastomeric plasticizer comprising components (b), (c) and (d), and admixing the plasticizer with the plastics component to form the desired composition.
12. A method according to claim 11 wherein the preformed elastomeric plasticizer comprises from 20 to 70 weight percent of component (b) and/or from 20 to 80 weight percent of olefinic elastomer component (c) and/or from 1 to 35 weight percent of hydrocarbon oil component (d), based on the plasticizer.

13. A method according to claim 11 or 12 wherein the preformed elastomeric plasticizer additionally includes up to 30 weight percent of an olefinic plastic, based on the plasticizer.
14. A method according to claim 13 wherein the olefinic plastic is selected from polypropylene, high density polyethylene and polypropylene reactor copolymer.
15. a method according to any one of claims 11 to 14 characterized in that said elastomeric plasticizer and said component (a) are each provided in pellet form.
16. A composition according to any one of claims 1 to 10 or produced according to the method of any one of claims 11 to 15 when in the form of a film.
17. A film when manufactured by producing a composition by the method of any one of claims 11 to 15 and performing a film forming step selected from cast extrusion, blown film tubular water bath extrusion, cast coextrusion, and extrusion coating.

0092318



European Patent
Office

EUROPEAN SEARCH REPORT

Application number

EP 83301625.6

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	<u>EP - A1 - 0 046 285</u> (MONTEDISON) * Claims * --	1	C 08 L 23/02 C 08 J 5/18
A	<u>EP - A1 - 0 041 937</u> (SEMPERIT) * Claims * --	1	
A	<u>EP - A2 - 0 032 804</u> (EXXON) * Claims * --	1,17	
D,A	<u>US - A - 4 132 698</u> (GESSLER) * Claims * --	1	
D,A	<u>US - A - 4 059 654</u> (V. BODUNGEN) * Claims * --	1	TECHNICAL FIELDS SEARCHED (Int. Cl. ³)
A	<u>DE - A - 2 204 239</u> (REIFENHÄUSER) * Claims * -----	1,16,17	C 08 L 23/00 C 08 J C 08 K
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
VIENNA	06-07-1983	TENGLER	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone			
Y : particularly relevant if combined with another document of the same category			
A : technological background			
O : non-written disclosure			
P : intermediate document			